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## Esterification and transesterification of waste cooking oil over Amberlyst 15 and modified Amberlyst 15 catalysts



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#### ABSTRACT

Biodiesel production via the simultaneous esterification and transesterification reactions of waste cooking oil (WCO) with methanol was investigated. A batch reflux reactor was used in conjunction with acidic ion-exchange catalysts, i.e., Amberlyst 15 and modified Amberlyst 15. The activity of the Amberlyst 15 catalysts could be altered via heat treatment at temperatures that are ≥493 K, as a consequence of the reduction of the active surface (-SO<sub>3</sub>H). The hydrogen ion-exchange capacities of the catalysts ranged from  $2.5 \text{ meq H}^+/\text{g}$  to  $5.1 \text{ meq H}^+/\text{g}$ . The reaction parameters included the molar ratio of alcohol to oil (6:1–15:1), reaction temperature (298–338 K), catalyst concentration (1–9 wt.%), reaction time (1–72 h) and the free fatty acid content (1.04-8.04%). It was observed that the activities of the Amberlyst 15 and modified Amberlyst 15 catalysts increased linearly with increasing hydrogen ion-exchange capacities of the catalysts. Amberlyst 15 exhibited the highest hydrogen ion-exchange capacity and consequently generated the highest biodiesel yield of  $(78 \pm 3.39\%)$ . The esterification reaction of excess fatty acids was also investigated. When the esterification and transesterification reactions were carried out simultaneously, the water generated from the esterification of free fatty acids led to the hydrolysis of triglycerides and reduced the biodiesel yield emphasizing the necessity for the removal of the water during concomitant esterification of excess fatty free acids present and the transesterification of the triglycerides for biodiesel production.

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#### 1. Introduction

Biodiesel is a renewable substitute diesel fuel that is manufactured from agricultural oils, animal fats and recycled cooking oils. Biodiesel is obtained from the transesterification of triglyceride molecules of oils/fats into lower alkyl esters of long chain fatty acids (fatty acid methyl ester (FAME) when vegetable oils are used) or the esterification of fatty acids [1]. Four different transesterification methods are available, i.e., base-catalyzed, acid-catalyzed, enzyme-based and non-catalytic transesterification under supercritical alcohol conditions [2–6]. The commercial manufacture of biodiesel from refined/edible type oils relies on the use of strongly basic (i.e., NaOH and KOH) or acidic solutions (H<sub>2</sub>SO<sub>4</sub>) as catalysts for the transesterification of triglycerides (TG) with monohydric alcohols, typically methanol [7]. Such homogeneous catalysts are generally corrosive to processing equipment. Homogeneous

catalysts can lead to the hydrolysis of oils and fatty acid methyl esters, depending on the water content of the feedstock [8-10].

The cost of biodiesel is still relatively high in comparison to petroleum-based diesel fuel. To reduce costs inexpensive feed stocks such as waste cooking oil can be used as raw materials [11-16]. The utilization of waste cooking oils as feedstock for biodiesel manufacture also has the potential of solving the problem of waste oil disposal. However, when the waste cooking oils contain total free fatty acid, FFA, contents >1 wt.% soap formation occurs under homogeneous alkaline catalysis [2,6,17,18]. To address the conversion of waste oils with high FFA contents, a two-step esterification process was developed [19]. In the first step FFA can be converted to fatty acid methyl esters and water via the use of a liquid acid catalyst such as sulfuric acid and in the second step transesterification is carried out by using alkaline catalysts to complete the reaction [13,19,20]. Acid catalysts can simultaneously catalyze both esterification and transesterification reactions, i.e., the esterification reaction for reducing the FFA level of oil and transesterification reaction for converting fatty acid into fatty acid methyl esters. However, acid

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catalyzed transesterification is not feasible since the homogeneous acid-catalyzed reaction is about 4000 times slower than the homogeneous alkaline-catalyzed transesterification reaction. Furthermore, such homogeneous acid catalyzed biodiesel production suffers from corrosion of equipment and the necessities of distillation for water removal, recycling of excess alcohol, and purification step for the product esters [21–24]. Replacement of the homogeneous acid catalysts with heterogeneous acid catalysts has the potential to overcome these drawbacks, to possibly render feasible the one step transformation of high FFA containing feedstocks into biodiesel. Indeed, recent investigations have demonstrated that the use of various heterogeneous catalysts based on super acids such as tungsten oxide, zirconia, zeolites, heteropolyacids, heteropolyacids immobilized on silica and clay-based catalysts can be used as solid acid catalysts for biodiesel production [7,10,15,25–38].

Acidic ion-exchange resins with their -SO<sub>3</sub>H groups have also been used for catalyzing the esterification reactions [39]. It has been demonstrated that the catalytic activity of acidic ion exchange resins increases nonlinearly with the concentration of sulfonic acid groups [39]. Strong acidic ion-exchange resins such as Amberlyst-15 were found to be effective catalysts for the esterification of free fatty acids and transesterification of oils [31,40–42]. Other ion-exchange resins (anionic Amberlyst A26 and A27 and cationic Amberlyst 15) were used as catalysts during the batch and continuous transesterification reactions to produce ethyl oleate as a biodiesel [41]. The anion exchange resins were found to have much higher catalytic activities than the cationexchange resins [41]. It was also determined that increases in the cross-linking density and particle sizes of anion exchange resins lead to lower conversions [41]. The catalytic activities of various mesoporous polymer-based solid acid catalysts were tested for biodiesel synthesis via transesterification and esterification of a mixture of tripalmitin and lauric acids with methanol [42].

Overall, although different types of ion-exchange resin catalysts were tested for use in esterification and transesterification reactions for biodiesel manufacture [31,40–42] systematic studies focusing on the use of ion-exchange resins with different acidities (i.e., hydrogen ion-exchange capacity, meqH<sup>+</sup>/g, values) were not carried out. Here a strong acidic ion-exchange resin, i.e., Amberlyst 15 was modified via heating to generate modified Amberlyst 15 catalysts with different hydrogen ion exchange capacities. A similar approach, based on the modification of Amberlyst 15 resin, was applied earlier for the etherification of isoamylenes [43].

The objectives of the investigation were to prepare a series of Amberlyst 15 based catalysts with differing hydrogen ion-exchange capacities and the assessments of their efficacies for esterification of the free fatty acids and the transesterification of the waste vegetable cooking oil (to be referred to as "oil") for biodiesel manufacture. The parameters of the reactions were the molar ratio of alcohol to oil (6:1–15:1), reaction temperature (298–338 K), catalyst concentration (1–9 wt.%), reaction time (1–48 h) and free fatty acid content (1.04–8.04%). The reusability of the Amberlyst 15 resin catalysts was also investigated.

#### 2. Experimental section

#### 2.1. Materials

Amberlyst 15 is a strongly acidic, macroreticular catalyst that is prepared from cross-linking of styrene with divinyl benzene and sulfonation with  $-SO_3H$ . The active sites of the catalyst arise from the sulfonic groups ( $-SO_3H$ ) which exhibit strong proton donor–acceptor properties. The Amberlyst 15 used in our investigation was obtained (Sigma-Aldrich, 216380) in the form of spherical beads. Amberlyst 15 was dried at 373 K overnight prior to use. Amberlyst 15 is reported to be thermally stable up to 393 K and its hydrogen ion-exchange capacity is 5.1 meq H+/g [43].

Analytical-grade methanol (purity 99.8 vol.%) was obtained from Riedel-de Haën (24228). Waste cooking oil (sunflower oil) was procured locally. The oil was filtered with a fine-mesh strainer to remove its solid content (particles >75 micron meter in size) and was kept at 100 °C for 1 h for the evaporation of its water. The free fatty acid concentration and the acid value of the waste cooking oil were determined as 1.04 wt.% and 2.08 mg KOH/g, respectively, following the AOCS Official Method Cd 3a-63 [44]. Oleic acid (Sigma-Aldrich, W281506) was added to the oil to facilitate the systematic investigation of the effects of changes in the free fatty acid concentration on esterification efficiencies of the catalysts.

#### 2.2. Catalyst preparation and characterization

Modified Amberlyst 15 catalysts were prepared by heating Amberlyst 15 at 493 K for different durations (4, 24, and 48 h). In an earlier study we have demonstrated that such thermal treatment alters the availability of sulfonic groups on Amberlyst 15 [43].

Various physical properties and hydrogen ion-exchange capacities of modified Amberlyst-15 catalyst particles are summarized in Table 1. The methods used in the characterization of these properties are provided elsewhere [43]. Upon heat treatment the hydrogen ion-exchange capacity of Amberlyst 15 decreased significantly with time. The rate of change of the hydrogen ion-exchange capacity with time diminished after 4 h.

The surface features of the Amberlyst 15 and modified Amberlyst 15 particles were documented using a Jeol\_JSM\_6400 Scanning Electron Microscope. Typical micrographs are shown in Fig. 1. Prior to heat treatment the catalyst surfaces were relatively smooth and largely free of macrocracks (Fig. 1a and b). With heat treatment the number and severity of surface macrocracks increase (Fig. 1c-f). Furthermore, upon heating the Amberlyst 15 particles become darker by assuming a brownish color.

#### 2.3. Esterification and transesterification reactions

The esterification and the transesterification reactions between the oil and methanol in the presence and absence of excess free fatty acids were performed in a batch reactor (Scheme 1). The reaction equipment consisted of a 250 ml three necked glass flask equipped with a water reflux condenser, a temperature-controlled magnetic

 Table 1

 Porosity, surface area and hydrogen ion-exchange capacities of Amberlyst 15 and modified Amberlyst 15 catalysts designated as 15-1 to 15-3.

| Catalyst | Duration of heat<br>treatment at 220 °C (h) | Hydrogen ion-exchange capacity* (meq H*/g) | $Porosity^{^{\circ}}, \varepsilon_a$ | BET surface<br>area* (m²/g) |
|----------|---|--|--------------------------------------|-----------------------------|
| Amb-15   | 0   | $5.1 \pm 0.14$                             | $0.32 \pm 0.01$                      | 39.0 ± 1.13                 |
| Amb-15-1 | 4   | $3.4\pm0.23$                               | $0.39 \pm 0.01$                      | $45.0 \pm 0.86$             |
| Amb-15-2 | 24  | $2.8 \pm 0.18$                             | $0.37 \pm 0.03$                      | $48.0\pm0.65$               |
| Amb-15-3 | 48  | $2.7\pm0.09$                               | $0.42\pm0.02$                        | $51.0 \pm 1.18$             |

The values in the table were found to be consistent with our previous study [43].

<sup>\*</sup> All data points are reported on the basis of measurements in triplicate and 95% confidence intervals, determined according to Student's-t distribution.

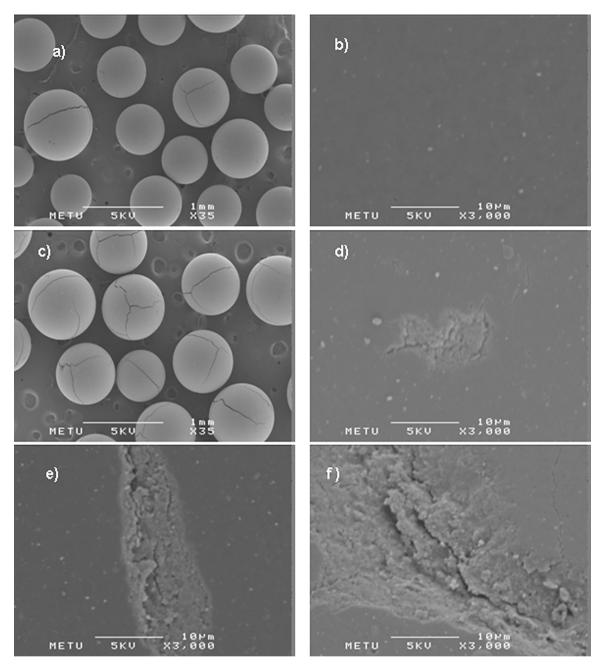


Fig. 1. SEM photographs (a) Amberlyst 15 (unmodified); (b) Amberlyst 15 (unmodified); (c) Amb-15-1; (d) Amb-15-1 (e) Amb-15-2; (f) Amb-15-3 (all micrographs were obtained prior to reaction).

stirrer and a sampling port. For the transesterification reactions a 50 g sample of the oil was charged to the three necked glass flask and was heated up to the desired temperature, while stirring at 600 rpm. Methanol and the solid acidic catalyst were premixed prior to being added into the batch reactor which contained the oil sample at the desired temperature. To investigate the esterification reaction in parallel with the transesterification reaction various quantities of excess free fatty acid were also introduced into the reactor.

All experiments were performed at atmospheric pressure. The transesterification experiments in the absence of excess fatty free acids were carried out at various molar ratios of alcohol/oil, i.e., between 6:1 to 15:1 and using a reaction time of 9 h. The reaction temperatures were 298, 318, 333, and 338 K. At the end of 9 h the reaction mixture was charged to a separating funnel and was

kept there overnight for the separation of glycerol and methyl ester phases.

The conversion of the triglycerides was determined following the AOCS Official Method Ca 14–56 [45]. According to this method the conversion of triglyceride (TG) is defined as:

$$X_{TG} = \frac{TG \text{ (in oil)} - TG \text{ (in ester)}}{TG \text{ (in oil)}}$$
(1)

Chemical analysis of the methyl esters (yield of biodiesel, %) was performed using an Agilent 6890 gas chromatograph (GC) equipped with a flame ionization detector and a capillary column CARBOWAX 20M. Sample preparation and GC analysis were carried out following European Standard of EN 14103 [46]. All data points are reported on the basis of measurements in triplicate

**Scheme 1.** The esterification (a) of oleic acid and the transesterification (b) reactions of triglyceride with methanol.

**Table 2**Effects of methanol/oil molar ratio on the yield of methyl ester and the conversion of triglyceride.

| Methanol/oil ratio (molar) | Conversion of triglyceride (%), $X_{TG}$ | Yield of biodiesel (%) |  |
|----------------------------|--|------------------------|--|
| 6:1                        | $52 \pm 1.25$                            | 62 ± 1.21              |  |
| 9:1                        | $55\pm1.27$                              | $66 \pm 1.25$          |  |
| 12:1                       | $64\pm2.85$                              | $78 \pm 3.39$          |  |
| 15:1                       | $63\pm2.20$                              | $77\pm2.22$            |  |

FFA level of the oil was 1.04% and the reaction conditions were: temperature: 338 K, catalyst concentration: 3 wt.%, reaction time: 9 h, catalyst type: unmodified Amberlyst 15.

and 95% confidence intervals, determined according to Student's-*t* distribution. All reported conversions are based on weight.

#### 3. Results and discussion

#### 3.1. Transesterification reaction

#### 3.1.1. The effects of methanol/oil molar ratio

The stoichiometric ratio for transesterification requires three moles of alcohol per mole of triglyceride to yield three moles of fatty acid methyl esters and one mole of glycerol. However, generally a large excess of alcohol is required to derive the reaction to the right, as shown in Scheme 1b. For such large excess of methanol significant concentrations of diglycerides and monoglycerides are not present in the product of the transesterification reaction [48].

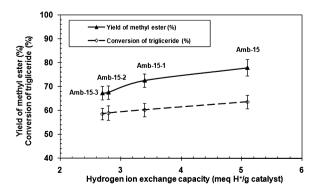
In our experiments with the Amberlyst 15 catalyst the methanol/oil ratios were 6:1,9:1,12:1 and 15:1. These experiments were carried out at 338 K at a catalyst concentration of 3 wt.% and a reaction time of 9 h. Methanol is not miscible with triglycerides at ambient temperature and thus the reaction mixture had to be continuously agitated to overcome mass transfer limitations found under quiescent conditions [1]. As seen in Table 2, the conversion of the triglycerides increased slowly with increasing methanol/oil ratios from 6:1 to 12:1. A maximum biodiesel yield of  $78\pm3.39$  was obtained at the methanol/oil ratio of 12:1. At the methanol/oil molar ratio of 15:1 some of the glycerol remained in the biodiesel phase and rendered the separation of glycerol difficult. Consequently the methyl ester yield decreased at the methanol/oil molar ratio of 15:1 (Table 2).

#### 3.1.2. The effects of the ion-exchange capacity of Amberlyst 15

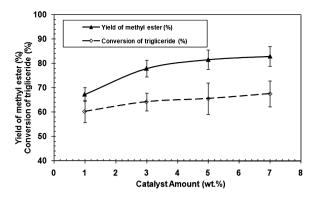
The effects of the hydrogen ion-exchange capacity of the Amberlyst 15 catalyst on transesterification reaction were investigated at 338 K, using a methanol/oil ratio of 12:1 and a catalyst concentration of 3 wt.%. The reaction time was 9 h. The FFA concentration of the oil was 1.04%. The ion-exchange capacities of Amberlyst 15 and the modified Amberlyst 15 catalysts (Amb-15-1, Amb-15-2 and Amb-15-3) ranged between 2.7 and 5.1 meg  $H^+/g$ (Table 1). As shown in Fig. 2, conversion of triglyceride and the yield of methyl ester increased with the increase of the hydrogen ion-exchange capacity of Amberlyst 15. However, the rate of the increase decreased with increasing ion-exchange capacity suggesting asymptotic behavior. The conversion of triglyceride was found to be approximately 15% lower that yield of methyl ester. Vegetables oil has 90-98% of triglycerides originally. However used cooking oil has much lower triglyceride concentrations depending on the source because of high heat treatment during usage.

#### 3.1.3. The effects of catalyst concentration

The effects of the concentration of the Amberlyst 15 catalyst (1, 3, 5 and 7 wt.% of the reaction mixture) on the yield of methyl ester and conversion of triglyceride were investigated. The FFA level of the oil was 1.04% and the reaction time, temperature and the alcohol/oil ratio were kept constant at 9 h, 338 K and 12/1, respectively. As shown in Fig. 3, the conversion of the triglycerides and the biodiesel yield increased with the increase of catalyst concentration, as expected. However, the sensitivity to the catalyst



**Fig. 2.** Hydrogen ion-exchange capacity dependency of the conversion of triglyceride to methyl ester and yield of methyl ester (*T*: 338 K, methanol/oil molar ratio: 12/1, catalyst amount: 3 wt.%, reaction time: 9 h).



**Fig. 3.** The effects of the concentration (weight percent) of the Amberlyst 15 catalyst in the reaction mixture for molar methanol/oil ratio of 12/1, temperature of 338 K and reaction time of 9 h.

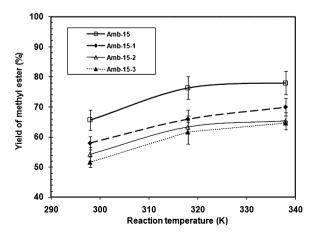
concentration diminished above 3% suggesting that asymptotes were reached. The significant increase of the yield of methyl esters between 1% and 3% catalyst amount is associated with the increase of the number of acid sites (hydrogen ion exchange capacity) of the Amberlyst 15 catalyst. Upon further increases of the catalyst amount the methyl ester yield reaches a plateau, suggesting that the equilibrium condition is already reached.

#### 3.1.4. The effects of reaction temperature

The effects of reaction temperature in the range of 298 to 338 K were investigated for Amberlyst 15 and modified Amberlyst 15 catalysts. In these experiments the methanol/oil molar ratio was kept at 12:1, the catalyst concentration was 3 wt.% and the reaction time was 9 h. As shown in Fig. 4, a maximum biodiesel yield of  $78\pm3.39\%$  was obtained over Amberlyst 15 catalyst at 338 K. The yield of the methyl ester increased significantly going from 298 to 318. Amberlyst 15 catalyst, having highest hydrogen ion-exchange capacity, generated the highest biodiesel yield at all temperatures. Increasing of the temperature above 318 K did not make a difference.

#### 3.1.5. The effects of free fatty acid level

It is known that both the esterification of free fatty acids and the transesterification of triglycerides can be catalyzed with sulfonic or sulfuric acids. Since Amberlyst 15 has —SO<sub>3</sub>H active groups it also has the potential to catalyze both the esterification and transesterification reactions [31,47,49,50].



**Fig. 4.** Dependence of the methyl ester yield on the reaction temperature over Amberlyst 15 and modified Amberlyst 15 catalysts (methanol/oil molar ratio: 12/1, catalyst concentration: 3 wt.%, reaction temperature: 338 K, reaction time: 9 h).

To evaluate the effects of the concentration of the free fatty acid in waste cooking oil on the conversion of triglycerides, different amounts of oleic acid (instead of the palmitic acid that was used in other investigations [19]) were added to the waste cooking oil The alcohol/oil ratio was kept at 12/1, and the concentration of the Amberlyst 15 catalyst, the reaction temperature and time were kept at 3 wt.%, 338 K and 9 h, respectively. The conversion of FFA (%) was calculated on the basis of the acid value of the oil prior to the reaction and the acid value of the ester phase after the reaction to biodiesel:

Conversion of FFA(%)

$$= \frac{\text{acid value (before reaction)} - \text{acid value (after reaction)}}{\text{acid value (before reaction)}} \times 100$$
 (2)

The data shown in Table 3 indicate that the biodiesel yield decreased with increasing of the free fatty acid concentration in the oil. The conversion of FFA was found to be more or less constant around 40% for the entire initial FFA concentration range of 1.04 to 8.04%. The catalytic activity of Amberlyst 15 is observed to decrease with the increasing concentration of the free fatty acid in the oil

Scheme 1 shows the esterification reaction (a) and the overall transesterification reaction (b). Scheme 2 shows that the reactions occur in the presence of water such as hydrolysis of triglycerides (a), and transesterification of triglycerides with oleic acid (b) over solid acidic Amberlyst 15 catalyst.

In general the esterification reaction is a faster reaction in comparison to the transesterification reaction [51]. Furthermore. water is generated as a byproduct of the esterification reaction (see Scheme 1a). Thus, when the FFA concentration increased (Table 3), a lower biodiesel yield was observed due to the increase in the amount of water produced during the esterification of FFA which prevented further transesterification reaction (Scheme 1b). Water generated as a result of the esterification reaction hydrolyzes the triglycerides, i.e., three moles of carboxylic acid (FFA) and one mole of glycerol is obtained (Scheme 2a). It can be hypothesized that water is adsorbed on the surface and within the pores of Amberlyst 15 and that this coating prevents the oil from reaching the catalyst surface. Thus, water has the potential to poison the Amberlyst 15 catalyst and consequently the biodiesel production efficacy would decrease. Similar conclusions are reached in other studies regarding acid catalyzed systems over Amberlyst 15 resins [47] and Lewis acid catalysts [52].

The mechanism for the transesterification reaction over acidic Amberlyst 15 catalyst is also provided in Scheme 3.

#### 3.2. Reusability of catalyst

The loss of catalyst activity upon reuse, i.e., the "reusability" of the catalyst, is an important parameter for the heterogeneous catalysis in transesterification reactions. A series of transesterification reactions were carried out using a constant set of operating conditions. Following each experiment the catalyst particles were separated from the reaction mixture by centrifuging, and were washed with methanol and *n*-hexane to remove both polar and non polar compounds adsorbed on the catalyst particles during the transesterification reaction. The catalyst particles were dried at 373 K prior to being reused. Reusability studies were carried out for Amberlyst 15 at molar methanol/oil ratio of 12/1, catalyst concentration of 3 wt.%, temperature of 338 K. Three successive 9 h reaction cycles were carried out. The methyl ester yields following recycling are shown in Table 4. The methyl ester yield is observed

#### a) Hydrolysis of triglycerides in the presence of water gives carboxylic acids

#### b) Transesterification of triglycerides in the presence of oleic acids gives carboxylic acid

**Scheme 2.** Hydrolysis of triglycerides (a) and transesterification of triglyceride with oleic acid.

Scheme 3. Possible acid catalyzed transesterification reaction mechanism over Amberlyst 15 (active sites: —SO<sub>3</sub>H).

**Table 3**The effects of free fatty acids on the conversion of triglyceride, the yield of methyl ester and conversion of FFA.

| Waste cooking oil | Oleic acid added<br>(wt.%) | FFA (%) | Before reaction          | After reaction           | Conversion of<br>FFA (%) | Conversion of triglyceride (%), $X_{TG}$ | Yield of methyl<br>ester (%) |
|-------------------|----------------------------|---------|--------------------------|--------------------------|--------------------------|--|------------------------------|
|                   |                            |         | Acid value<br>(mg KOH/g) | Acid value<br>(mg KOH/g) |                          |  |                              |
| WCO               | _                          | 1.04    | 2.08                     | 1.22                     | 41                       | $64 \pm 2.85$                            | 78 ± 3.39                    |
| WCO-1             | 1                          | 1.83    | 3.66                     | 2.23                     | 39                       | $59 \pm 2.85$                            | $70 \pm 2.85$                |
| WCO-5             | 5                          | 5.43    | 10.86                    | 6.32                     | 42                       | $53 \pm 2.85$                            | $62 \pm 2.85$                |
| WCO-10            | 10                         | 8.04    | 16.08                    | 9.05                     | 44                       | $49 \pm 2.85$                            | $58 \pm 2.85$                |

(Reaction conditions: methanol/oil: 12:1, T: 338 K, catalyst concentration: 3 wt.%, reaction time: 9 h, catalyst type: unmodified Amberlyst 15).

**Table 4**Reusability of Amberlyst 15 catalyst<sup>\*</sup>.

| Runs    | Yield of methyl ester (%) |  |
|---------|---------------------------|--|
| 1st use | 78 ± 3.39                 |  |
| 2nd use | $78 \pm 1.20$             |  |
| 3rd use | $77 \pm 1.50$             |  |

\* Reaction conditions: methanol/oil: 12/1, temperature: 338 K, reaction time: 9 h, catalyst amount: 3 wt.%.

not to depend on recycling and at least for two additional catalysis runs, suggesting that no significant loss of catalytic activity of Amberlyst 15 for at least three cycles of reuse. These results are consistent with the investigation of Dong et al., whereby Amberlyst 15 was recycled 8 times for biodiesel production from microalgae with high free fatty acid content and no significant loss of activity was observed [49].

#### 4. Conclusions

Amberlyst 15 and modified (heat treated) Amberlyst 15 catalysts were used for the transesterification of triglycerides and the esterification of free fatty acids FFA found in waste vegetable cooking oils with methanol. The heat treatment decreased the hydrogen ion-exchange capacity of Amberlyst 15 and led to the deterioration of the methyl ester yield upon transesterification. Without heat treatment and modification Amberlyst 15 catalysts could generate a methyl ester yield of 78% following 9 h at 338 K, under a methanol/oil ratio of 12:1 and using a Amberlyst 15 catalyst concentration of 3 wt.%. Thus, a high hydrogen ion exchange capacity is essential for the catalytic activity of Amberlyst 15 catalysts for transesterification. It is shown that Amberlyst 15 also has the potential to reduce the FFA level in the waste oil. However, a constant FFA conversion of 40% was observed for all FFA levels, and it is hypothesized that the water, generated as a by-product of the esterification reaction of FFA, is poisoning the Amberlyst 15 catalyst suggesting that the concomitant esterification and transesterification reactions with Amberlyst 15 would be only feasible if the water that is generated is continuously removed from the reaction mixture. The catalytic activity of Amberlyst 15 did not deteriorate after reuse at least for the three cycles that were applied.

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